SCIENTIFIC **Reports**

Received: 28 June 2015 Accepted: 09 October 2015 Published: 04 November 2015

OPEN Strain assisted electrocaloric effect in PbZr_{0.95}Ti_{0.05}O₃ films on 0.7Pb(Mg_{1/3}Nb_{2/3})O₃-0.3PbTiO₃ substrate

Zhenghu Zuo^{1,2}, Bin Chen^{1,2}, Baomin Wang^{1,2}, Huali Yang^{1,2}, Qingfeng Zhan^{1,2}, Yiwei Liu^{1,2}, Junling Wang^{1,3} & Run-Wei Li^{1,2}

Solid state cooling technologies based on electrocaloric, magnetocaloric and mechanocaloric effects have received much attention during the past decade. To further improve the cooling efficiency and reduce the driving field, it is desirable to combine multiple effects in a single system. Here, we report on the caloric effects induced by both electric field and strain in PbZr_{0.95}Ti_{0.05}O₃ films deposited on 0.7Pb(Mq_{1/3}Nb_{2/3})O₃-0.3PbTiO₃ substrate. The isothermal entropy change (ΔS) induced by the antiferroelectric-ferroelectric phase transition of $PbZr_{0.95}Ti_{0.05}O_3$ films is calculated to be 6.78 J K⁻¹ kg⁻¹. Furthermore, the strain from 0.7Pb(Mg_{1/3}Nb_{2/3})O₃-0.3PbTiO₃ substrate can reduce the electric field where ΔS reaches the maximum by as much as 50 kV/cm. The electrocaloric efficiency is also increased from 0.366 to 0.378 by the strain effect. The electrocaloric effect in an antiferroelectric material assisted by strain may lead to more efficient solid state cooling technology.

The search for a highly efficient and environmentally friendly solid state cooling technology has attracted much attention recently¹⁻⁹. It offers an alternative to the traditional vapor-compression cooling method widely used in household and industrial applications, which involves hazardous gases. Several technologies that are currently being developed make use of various caloric effects, i.e. electrocaloric (EC), magnetocaloric (MC), and/or mechanocaloric (mC) effect. Caloric effect refers to a change in temperature under adiabatic application of external fields. Alternatively, it can be described as an isothermal change in entropy. To achieve a large caloric effect, a phase transition is desirable where the entropy change (ΔS) is maximized. For example, the giant mC, MC, and EC effects observed in the shape memory alloy Cu_{69.6}Al_{27.7}Ni_{2.7}⁷, the metallic Fe₄₉Rh₅₁⁸, and the ceramic PbZr_{0.95}Ti_{0.05}O₃ (PZT)⁹ are associated with martensite-austenite, antiferromagnetic-ferromagnetic, and ferroelectric-paraelectric phase transitions, respectively. Each of these caloric effects is induced by a particular driving field. Moving forward, it is natural to investigate caloric effects driven by multi-fields for better performance, as proposed by Moya et al. in a recent review¹.

It is well known that the ferroic phase transition usually leads to a large change in entropy². In 2006, large EC effect was observed experimentally in ferroelectric PZT⁹. Recently, a theoretical study has shown that giant mC can be expected in ferroelectric Ba_{0.5}Sr_{0.5}TiO₃¹⁰ and BaTiO₃¹¹. However, there are few experimental reports on caloric effects driven by multi-fields up to now¹². In this paper, we report the caloric effect driven by both electric field and strain in antiferroelectric PZT films on 0.7Pb(Mg_{1/3}Nb_{2/3})

¹Key Laboratory of Magnetic Materials and Devices, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China. ²Zhejiang Province Key Laboratory of Magnetic Materials and Application Technology, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China. ³School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore. Correspondence and requests for materials should be addressed to B.W. (email: wangbaomin@nimte.ac.cn) or J.W. (email: JLWang@ntu.edu.sg) or R.-W.L. (email: runweili@nimte.ac.cn)





 O_3 -0.3PbTi O_3 (PMN-PT) substrate. The idea is that both the electric field applied to the films and the strain from the substrate can contribute to the ΔS of the PZT films. Indeed, a large ΔS of about 6.78 J $K^{-1}kg^{-1}$ can be obtained in the hybrid system.

Results

300 nm PZT films were prepared on (001) orientation PMN-PT substrates with 30 nm SrRuO₃ (SRO) bottom electrode by pulsed laser deposition (PLD). Figure 1a shows the XRD θ -2 θ pattern of the sample. In addition to the pseudo-cubic (200) peaks of the substrate and SRO layer, only peaks from the (200) and (002) planes of the tetragonal PZT can be seen, which demonstrates that 90° *a*-*c* domains are present in the film. It can also be seen that the films are *a*-domain dominated. The AFM image of the PZT film is displayed in the inset of Fig. 1a, which shows that the roughness is very small (~3 nm). The electric field dependence of polarization (*P*-*E* loop) of the PZT films at room temperature is shown in Fig. 1b, typical of an antiferroelectric material.

The caloric effect of meta-magnetic materials at the magnetic transition has been reported extensively^{1,13}. Similarly, ΔS also occurs at the antiferroelectric-ferroelectric transition in antiferroelectric materials. In order to evaluate the caloric effect in the antiferroelectric PZT films, the *P*-*E* loops are measured at various temperatures between 270 K and 330 K and selected results are shown in Fig. 2a. From the *P*-*E* loops we can define a transition electric field, *E_t*, at each temperature. The polarization change, ΔP , at the transition can also be estimated from these curves. In the inset of Fig. 2a we show the transition field as a function of temperature. We see that *E_t* rises linearly with decreasing *T*, with a slope of dEt/dT = -0.94 kV/cm K.

The ΔS due to first-order phase transitions in magnetic materials and shape-memory alloys have been calculated by using the modified Maxwell functions^{6,14}. Assuming a system subjected to an electric field *E* undergoes a first-order phase transition in equilibrium at a temperature T_{ρ} the transition is



Figure 2. Temperature dependences of *P*-*E* loops and ΔS of PZT on PMN-PT at different electric fields. (a) *P*-*E* loops at selected temperatures. The inset shows the transition field as a function of temperature. The line is a linear fit $E_t = -0.94T + 851$. (b) Electric field induced ΔS at selected values of electric field ranging from 528 to 680 kV/cm.

characterized by discontinuities in variables such as polarization and entropy that are thermodynamically conjugated to the electric field and temperature. In the vicinity of the transition, the following behavior of the polarization is thus expected, $P(T, E) = P_0 + \Delta P \mathcal{F}[(T_t(E)-T)/\Delta T]]$, where \mathcal{F} is a shape-function and ΔT is the temperature range over which the transition spreads. In strict equilibrium, $\Delta T \rightarrow 0$ and \mathcal{F} approaches the Heaviside step function. Following the expression $\Delta S (0 \rightarrow E) = -\int_0^E \left(\frac{\partial P}{\partial T}\right)_E dE$ and assuming that P_0 and ΔP are constants, the caloric effect in the vicinity of the transition in this equilibrium case is given by

$$\Delta S(0 \to E) = \begin{cases} -\frac{\Delta P}{\alpha}, \ T \in [T_t(0), \ T_t(E)] \\ 0, \ T \notin [T_t(0), \ T_t(E)] \end{cases}$$
(1)

where $\alpha \equiv dT_t/dE$ is assumed to be constant. Taking into account the Clausius-Clapeyron equation, $\alpha = \Delta P/\Delta S_t$, where ΔS_t is the transition entropy change. Therefore, as expected $\Delta S (0 \rightarrow E) = \Delta S_t$, and $\Delta T = T_E - T_t(0) = \alpha E$. The caloric effect (electric field-induced ΔS) has been obtained by numerically computing the integral in Eq. (1). The result is shown in Fig. 2b. Note that the maximum ΔS of 6.78 J $K^{-1} kg^{-1}$ remains almost constant (thus independent of temperature and applied stress) over a very broad temperature range.

It is well known that the antiferroelectric-ferroelectric phase transition in antiferroelectric materials is usually accompanied by a large volume change¹⁵. During the phase transition, the lattice parameter *a* decreases while *c* increases. Therefore, if we apply a tensile strain in the (001) plane of the antiferroelectric films, E_t will increase. Conversely, the opposite occurs if we apply a compressive strain. Using



Figure 3. *P-E* loops of PZT on PMN-PT at 330K under different applied strains. The inset shows the electric field dependence of polarization and strain of PMN-PT substrate.



Figure 4. Electric field and temperature dependence of ΔS under different strains applied from PMN-PT substrate. (a) Electric field dependence of ΔS at two selected temperatures with and without applied strain. (b) Temperature dependence of ΔS at 624kV/cm with different strain applied.

PMN-PT as the substrate, we can apply electric field on the substrate to induce an in-plane tensile strain to the film. The tensile strain will reduce the E_t of PZT films because our samples are *a*-domain dominated as discussed above. The electric field dependence of polarization and strain of the PMN-PT substrate is shown in the inset of Fig. 3. The shift of loops is due to the asymmetric electrodes used. When the electrode generates an out-of-plane compressive strain of -0.05% (@ 4kV/cm), an in-plane tensile strain of 0.025% is induced. *P*-*E* loops of the PZT films at 330K under different strain states are shown in Fig. 3, from which we can see that the transition field of the PZT film shifts to a lower value when the strain becomes larger while the saturation polarization remains almost the same.

The electric field and strain induced ΔS at selected temperatures is shown in Fig. 4. We can see that when the electric field applied to PZT is lower than 512 kV/cm, the antiferroelectric-ferroelectric transition cannot occur. Therefore, the ΔS is zero. When the electric field is larger than 688 kV/cm, the transition is completed. As a result, the ΔS reach a maximum value. Compared to the transition caused by electric field only, the total ΔS induced by the combination of electric field and strain remains relatively unchanged. However, the strain reduces the electric field needed to achieve certain ΔS . For PZT films at 330 K, the electric field where ΔS reaches the maximum is reduced by ~ 50 kV/cm due to strain from the substrate. When we apply an electric field of 624 kV/cm to the PZT films, the ΔS at 270 K is about 3.2 J K⁻¹kg⁻¹ while the ΔS under a 0.025% strain is around 5.5 J K⁻¹kg⁻¹ (shown in Fig. 4b). At 330 K, the difference between different strain states is very small. Therefore, when a certain electric field lower than E_t is applied to the PZT films, external strain can result in larger ΔS over a wide temperature range. We have also considered the electrocaloric efficiency (η) of the hybrid system as introduced by Defay *et al.*¹⁶, which equals to the ratio of reversible electrocaloric heat (Q) to reversible electrocaloric work (W) under isothermal condition. The value of Q can be evaluated following $|Q|=T|\Delta S|$, while W can be

calculated following $|W| = |\int_{P_1}^{P_2} EdP|$. The calculated η is about 0.366 for the PZT film alone while it increases to 0.378 when -0.05% strain induced by PMN-PT is applied to the PZT film.

Discussion

For entropy change for ferroelectric to paraelectric transition, a large value could be only obtained around the Curie temperature (T_c). When the work temperature is away from the T_c , the entropy change will be very small. Therefore, the work temperature of the cooling device using ferroelectric to paraelectric transition was limited to the T_c of the functional material. However, a relatively large value of the entropy change for antiferroelectric to ferroelectric transition could be arrived over a wide range only if the work temperature is lower than the T_c of the functional material. Our findings are especially useful for bulk ferroelectric ceramic samples because they usually cannot withstand the high electric field that thin films can. With a pre-load strain, a lower electric field can result in larger ΔS , ideal for electrocaloric solid-state refrigeration technology¹⁷.

In conclusion, a large ΔS of 6.78 J K⁻¹ kg⁻¹ is obtained from the antiferroelectric-ferroelectric phase transition in PZT films induced by electric field and strain from the substrate. The strain helps to reduce the electric field needed to achieve maximum ΔS by as much as 50 kV/cm and increases the electrocaloric efficiency from 0.366 to 0.378. Furthermore, ΔS can be obtained in a broad range of temperatures which opens up interesting opportunities in refrigeration applications based on the caloric effect.

Methods

Specimen Fabrication. Pulsed laser deposition (PLD) was used to prepare the SrRuO₃ (SRO) bottom electrode and PZT film on (001) orientation PMN-PT substrate at 800 °C with an oxygen partial pressure of 10 Pa. After the deposition of PZT film, 100 nm Cu top electrodes of $100 \times 100 \,\mu\text{m}^2$ were grown by thermal evaporation using a metal mask.

Characterization. The surface morphologies of the as-grown films were studied using an atomic force microscopy (Dimension3100V, Bruker). The structure of the films were characterized using an X-ray diffraction (D8 Advance, Bruker). Ferroelectric properties were measured using a commercial ferroelectric tester (Precision Premier II, Radiant Technology).

References

- 1. Moya, X., Kar-Narayan, S. & Mathur, N. D. Caloric Materials near ferroic phase transitions. Nat. Mater. 13, 439-450 (2014).
- 2. Fahler, S. et al. Caloric effects in ferroic materials: New concepts for cooling. Adv. Eng. Mater. 14, 10–19 (2012).
- 3. Correia, T. Electrocaloric Materials (eds Correia, T. et al.) 1-15 (Springer, 2014).
- 4. Tishin, A. M. & Spichkin, Y. I. The Magnetocaloric Effect And Its Applications (ed. Spicer, T.) 1–3 (Taylor & Francis, 2003).
- 5. Manosa, L. et al. Giant solid-state barocaloric effect in the Ni-Mn-In magnetic shape-memory alloy. Nat. Mater. 9, 478-481 (2010).
- Bonnot, E., Romero, R., Manosa, L., Vives, E. & Planes, A. Elastocaloric effect associated with the martensitic transition in shapememory alloys. *Phys. Rev. Lett.* 100, 125901 (2008).
- 7. Bechtold, C., Chluba, C., De Miranda R. L. & Quandt, E. High cyclic stability of the elastocaloric effect in sputtered TiNiCu shape memory films. *Appl. Phys. Lett.* **101**, 091903 (2012).
- 8. Nikitin, S. A. et al. The magnetocaloric effect in Fe₄₉Rh₅₁ compound. Phys. Lett. A. 148, 363–366 (1990).
- Mischenko, A. S., Zhang, Q., Scott, J. F., Whatmore, R. W. & Mathur, N. D. Giant electrocaloric effect in thin-film PbZr_{0.95}Ti_{0.05}O₃. Science 311, 1270–1271 (2006).
- Lisenkov, S. & Ponomareva, I. Giant elastocaloric effect in ferroelectric Ba_{0.5}Sr_{0.5}TiO₃ alloys from first-principles. *Phys. Rev. B* 86, 104103 (2012).
- 11. Liu, Y. et al. Giant room temperature elastocaloric effect in ferroelectric ultrathin films. Adv. Mater. 26, 6132-6137 (2014).
- 12. Starkova, A. S. & Starkov, I. A. Multicaloric effect in a solid: New aspects. J. Exp. Theor. Phys. 119, 258–263 (2014).
- 13. Planes, A., Monosa, L. & Acet, M. Magnetocaloric effect and its relation to shape-memory properties in ferromagnetic heusler alloys. J. Phys.: Condens. Mater. 21, 233201 (2009).
- 14. Sun, J. R., Hu, F. X. & Shen B. G. Comment on "Direct measurement of the giant adiabatic temperature change in Gd₅Si₂Ge₂". *Phys. Rev. Lett.* **85**, 4191 (2000).
- Pan, W. Y., Dam, C. Q., Zhang, Q. M. & Cross, L. E. Large Displacement transducers based on electric field forced phase transitions in the tetragonal (Pb_{0.97}La_{0.02})(Ti,Zr,Sn)O₃ family of ceramics. J. Appl. Phys. 66, 6014–6023 (1989).
- Defay, E., Crossley, S., Kar-Narayan, S., Moya, X. & Mathur, N. D. The electrocaloric efficiency of ceramic and polymer films. *Adv. Mater.* 25, 3337–3342 (2013).
- 17. Valant, M. Electrocaloric materials for muture solid-state refrigeration technologies. Prog. Mater. Sci. 57, 980-1009 (2012).

Acknowledgements

The authors gratefully thank Dr. Xiao Long Li of SSRF for XRD measurements, and acknowledge the financial supports from the State Key Project of Fundamental Research of China (2012CB933004), National Natural Science Foundation of China (51402318, 11274321, 11274322, 51301191), China Postdoctoral Science Foundation funded project (2014M561525), Overseas, Hong Kong & Macao Scholars Collaborated Researching Fund (51428201), the Key Research Program of the Chinese Academy of Sciences (KJZD-EW-M05), Ningbo international cooperation projects (2012D10018) and Ningbo Major Project for Science and Technology (2014B11011).

Author Contributions

Z.Z., J.W. and R.L. conceived the experiments. Z.Z. and B.C. carried out experiments. Z.Z., J.W. and R.L. wrote the manuscript. B.W., H.Y., Q.Z. and Y.L. discussed the data and the results, and commented the manuscript.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Zuo, Z. *et al.* Strain assisted electrocaloric effect in $PbZr_{0.95}Ti_{0.05}O_3$ films on $0.7Pb(Mg_{1/3}Nb_{2/3})O_3-0.3PbTiO_3$ substrate. *Sci. Rep.* **5**, 16164; doi: 10.1038/srep16164 (2015).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/